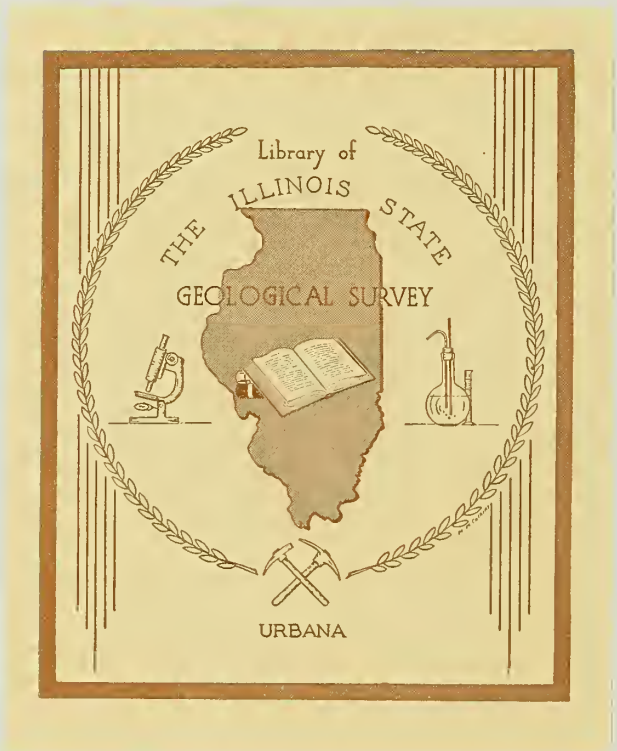

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MINERALOGY AND PETROGRAPHY OF CARBONATE ROCKS RELATED TO CONTROL OF SULFUR DIOXIDE IN FLUE GASES

a preliminary report

RICHARD D. HARVEY

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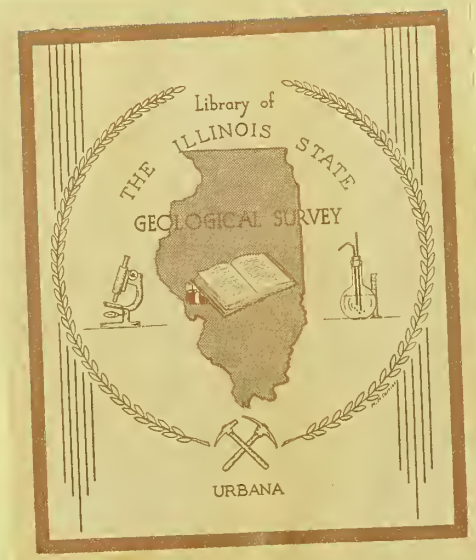
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MINERALOGY AND PETROGRAPHY OF CARBONATE ROCKS RELATED TO CONTROL OF SULFUR DIOXIDE IN FLUE GASES—

A Preliminary Report*

Richard D. Harvey

INTRODUCTION

The growing interest in reducing or eliminating air pollution has spurred research in many fields. The control of sulfur dioxide (SO_2) released into the air from electric power plants has received particular attention, and means of preventing this pollution are being sought. One process that has been given consideration (Wickert, 1963, Battelle Memorial Institute, 1966, and others) is based on the chemical reaction that occurs between solid particles of lime (CaO) and the gases sulfur dioxide (SO_2) and oxygen (O_2) in the temperature range of approximately 1200° to 1800° F to form particles of anhydrite:

$$CaO + SO_2 + \tfrac{1}{2}O_2 = CaSO_4.$$

Particles of calcium sulfite ($CaSO_3$) may form an intermediate step according to

$$CaO + SO_2 = CaSO_3$$
$$CaSO_3 + \tfrac{1}{2}O_2 = CaSO_4.$$

Magnesium oxide (MgO) reacts exactly as calcium oxide does to form magnesium sulfite ($MgSO_3$) and magnesium sulfate ($MgSO_4$). The calcium sulfate particles can be easily collected and disposed of. Magnesium sulfate, being soluble in water, would require special treatment to prevent pollution of streams and ground water.

Limestone consists mainly of calcium carbonate ($CaCO_3$) and dolomite of calcium magnesium carbonate ($CaMg(CO_3)_2$), and these rocks provide economical

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* Based on a paper presented at the Third Limestone Symposium sponsored by the U. S. Department of Health, Education, and Welfare, Public Health Service, St. Petersburg, Florida, December 4-8, 1967.

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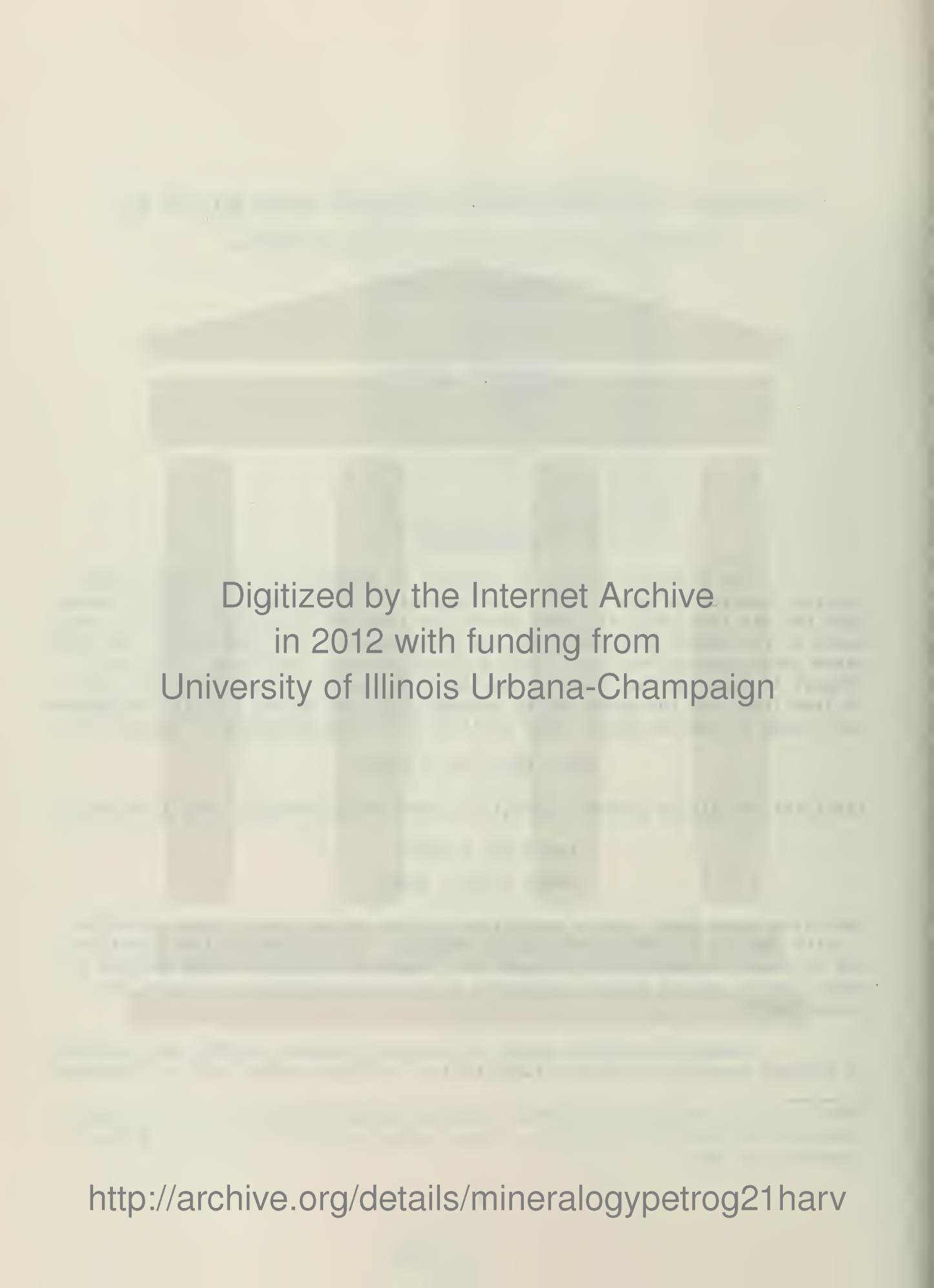
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sources of calcium and magnesium oxides for reaction with SO_2. The rocks can be pulverized and injected into the flue gases at the proper temperature to produce the required oxides by calcination. The oxides then react with SO_2 and O_2 to produce the disposable solids.

In predicting to what extent various types of limestones and dolomites will react with SO_2 in flue gases, the basic premise is that the higher the CaO and MgO contents of the stone, the greater will be its capacity to react with SO_2. Certain conditions can modify this premise. The first is that in any natural stone used, the calcium and magnesium must be bonded in carbonate minerals or they will not react with SO_2. Calcium and magnesium reported in chemical analyses as oxides may in fact be bonded in silicate minerals, in which case they will not form oxides under the conditions existing in flue gases. A second possible limitation to the premise is the effect of the presence of 1 to 2 percent iron oxide in the rock. Even though the CaO or MgO content is thereby somewhat reduced, the iron oxide may compensate for its presence by acting as a catalyst to promote the oxidation of the sulfur (Wickert, 1963, and Rees et al., 1966). The texture (the size, shape, and arrangement of grains) of the rock also may limit the direct application of the premise.

The object of my research program was to determine what important characteristics of naturally occurring carbonate rocks, if any, influence their SO_2 absorption capacity. To date, I have examined the mineralogical and petrographic characteristics of limestone and dolomite samples that previously had been tested for their sulfur oxide reactivity by Harrington, Borgwardt, and Potter (1967) in the laboratories of the National Center for Air Pollution Control, Public Health Service, U. S. Department of Health, Education, and Welfare.

The cooperation of Richard E. Harrington, Robert H. Borgwardt, and Allen E. Potter of the U. S. Public Health Service in supplying the samples and the sulfur reactivity data used in this study and their permission to use their data in this report are gratefully acknowledged.

SAMPLES STUDIED

Ten samples, two of them from Illinois limestones, were obtained for study from the U. S. Public Health Service, Cincinnati, Ohio. The samples were broken pieces of stone about 1 to 10 mm across. Thin sections of many pieces of each sample were studied with a polarizing microscope. Most of the remaining pieces were pulverized, and X-ray diffraction, carbon dioxide, and acid solubility analyses were made.

The samples were representative portions of larger samples that had been tested for their SO_2 absorption by the Public Health Service. In those tests, each sample was first calcined at 1800° F for 2 hours, after which sulfur absorption measurements were made on the calcined materials. The sulfur absorptive data were reported in terms of the "time to 20 percent breakthrough" (Harrington, Borgwardt, and Potter, 1967). This breakthrough time is the observed time required for 20 percent of the original amount of SO_2 that entered the sample chamber to pass through the sample unreacted. The greater the breakthrough time, the more SO_2 was absorbed by the sample. The breakthrough time was determined at various temperatures; however, the values reported in table 1 of this report are those given by Harrington and co-workers for the tests run at 1600° F.

TABLE 1 - MINERALOGICAL AND SULFUR ABSORPTION (20% BREAKTHROUGH TIME) DATA

Sample	Soluble in dilute HCl (%)	Quartz content (%)	Clay content (%)	Carbon dioxide content (%)	Calcite + dolomite + ≤5% limonite* (%)	20% breakthrough time † (min)
BCR 1362	84.5	7	7	34.2	77.9	29
BCR 1342[a]	88.0	-	-	38.6	83.5	35
BCR 1363	90.4	3	6	39.4	79.9	59
BCR 1352[b]	91.4	2	4	43.1	92.8	88
BCR 1343[b]	98.0	1	1	43.4	97.7	95
BCR 1361	92.1	4	4	40.5	93.1	110
BCR 1359	98.0	<1	<1	43.6	99.1	115
BCR 1337	99.0	<1	<1	47.4	99.3	119
BCR 1351	94.0	3	3	42.3	94.5	128
BCR 1360	95.0	5	<1	43.0	97.6	150

* Mineral percentages calculated from chemical analyses by Harrington, Borgwardt, and Potter, 1967, table 1.

† Data taken from Harrington, Borgwardt, and Potter, 1967, fig. 5 (1600° F).

[a] 5 percent diopside and 5 percent antigorite present in the sample.

[b] 1 percent pyrite, or less, present in the sample.

MINERALOGY OF THE SAMPLES

The weight percentages of the acid-soluble minerals (calcite + dolomite + limonite) determined in the samples studied are listed in table 1. The residues were mainly quartz (in the form of discrete sand-silt grains or as irregular masses of chert) and clay. The percentages of these minerals present in the samples are listed in table 1 to the nearest percentile. The specific types of clay minerals present were not determined. Small amounts of organic material were observed in the residues of samples BCR 1352 and BCR 1359.

PETROGRAPHY OF THE SAMPLES

Petrographic examination of thin sections of the samples revealed several different types of limestones and dolomites and a marble (table 2). The stones were classified on the basis of their major and minor mineral components. For instance, a stone containing a large amount of calcite and a smaller amount of dolomite was classed as dolomitic limestone. Stones in which fossils are very abundant were further classified as fossiliferous (BCR 1363 and 1343).

The grain-size distribution of a material has a definite bearing on the properties of the material and could be important in predicting the SO_2 capacity of the limestone or dolomite. Grain size is a complex petrographic factor in limestones because the grains frequently occur in a large range of sizes and shapes. To obtain an estimate, the predominant particle size of the

TABLE 2 - PETROGRAPHY OF SAMPLES

Sample*	Type of stone	Granularity	Predominant grain size†	Remarks
BCR 1362	ferruginous limestone	inequigranular	coarse	Hematitic fossils, sparry calcite cement, rust-coated fragments
BCR 1342	diopside-dolomitic marble	equigranular	medium	Fine-grained calcite abundant and fibrous antigorite present
BCR 1363	algal limestone	inequigranular	fine	Shale fragments present
BCR 1352	calcitic dolomite	equigranular	fine	Rhombic mosaic; organics along grain boundaries
BCR 1343	fossiliferous limestone	inequigranular	fine	Sparry calcite patches abundant, some areas recrystallized
BCR 1361	dolomitic limestone	inequigranular	fine	Rhombic mosaic patches of medium-grained dolomite scattered throughout the rock
BCR 1337	dolomite	equigranular	medium	Rhombic mosaic
BCR 1359	limestone	equigranular	fine	Some patches of sparry calcite present; organics occur along grain boundaries in some fragments
BCR 1351	calcitic dolomite	equigranular	fine	Weathered; some fragments very soft; limonite along grain boundaries
BCR 1360	dolomitic limestone	inequigranular	coarse	Coarse crinoid fragments set in fine- and medium-grained dolomitic matrix

* Samples supplied by U. S. Public Health Service.

† Fine: 4 to 63 microns, medium: 63 to 250 microns, coarse: > 250 microns.

grains present in the samples was determined with a microscope and these values were assigned to one of four size categories (table 2): (1) micro—less than 4 microns across, (2) fine—4 to 63 microns across, (3) medium—63 to 250 microns across, (4) coarse—over 250 microns across. None of the samples are micrograined.

The relative distribution of grain sizes in a rock is called its granularity (table 2). An equigranular rock is one in which the grains are all approximately the same size. "Inequigranular" refers to one in which one fourth to three fourths of the grains are noticeably larger than the others.

Additional remarks on the petrography of the samples are given in table 2. The term "sparry calcite" refers to clear, crystalline calcite that fills voids in fossils and former pore spaces between fossils and other types of particles. "Rhombic mosaic texture" refers to the occurrence of many grains with a rhombic shape and planar grain boundaries. This type of texture, is somewhat "loose" compared to the usual mosaic texture in which the grains have curvilinear boundaries and are tightly interlocked.

DISCUSSION

A comparison of the sulfur absorption capacities of the samples measured by the 20 percent breakthrough time and mineral content is shown graphically in figures 1, 2, and 3. Figure 1 shows the breakthrough times versus the CO_2 content of the samples. A fairly linear distribution of the datum points indicates a good correlation between the two sets of values.

Figure 2 shows the breakthrough times versus the percentage of the samples soluble in warm, dilute HCl. With increasing solubility in HCl there is a rapid increase in breakthrough time. As the soluble minerals in the samples are calcite, dolomite, and limonite, the correlation in figure 2 can be checked with the chemical analysis of the samples (Harrington, Borgwardt, and Potter, 1967, table 1). From these analyses the mineral content may be calculated by using ideal mineral formulas. The graph of the sum of the calculated percentages of calcite, dolomite, and as much as 5 percent of the limonite in the samples plotted against the sulfur dioxide breakthrough time (fig. 3) also shows a correlation similar to that in figure 2. A maximum value of 5 percent limonite was chosen because a greater amount of limonite (and hematite) appears to dilute significantly the CaO and MgO of the reacting sample (sample BCR 1362).

An evaluation of the dolomite content can be made from the data presented in figure 3. The shaded area of the datum points is proportional to the dolomite content of the sample. The amount of dolomite present in the sample does not appear to affect the time to breakthrough as there is no systematic distribution of points and their shaded portions. These results show that, as premised, the greater the percentage of calcium and magnesium carbonates in the rock the greater will be the reactivity with SO_2.

The influence of petrographic texture on SO_2 reactivity is not clearly indicated by the data. The predominant grain size of the samples is indicated on figure 3. For samples with less than 5 percent impurities, the two fine-grained samples had the shortest breakthrough times (BCR 1343 and 1359). The coarsest grained sample (BCR 1360) had the longest breakthrough time, and the

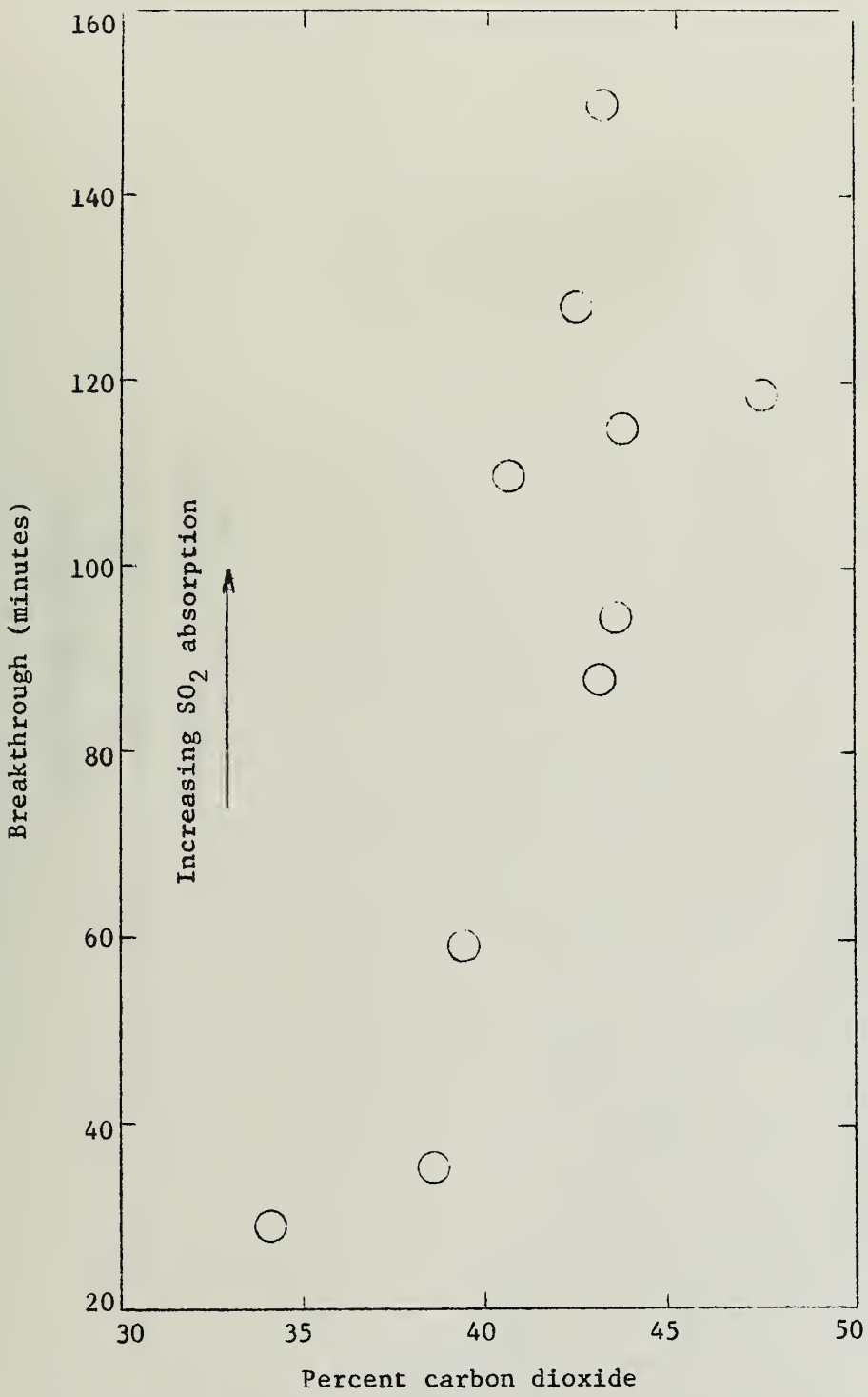

Fig. 1 - Breakthrough time versus carbon dioxide content.

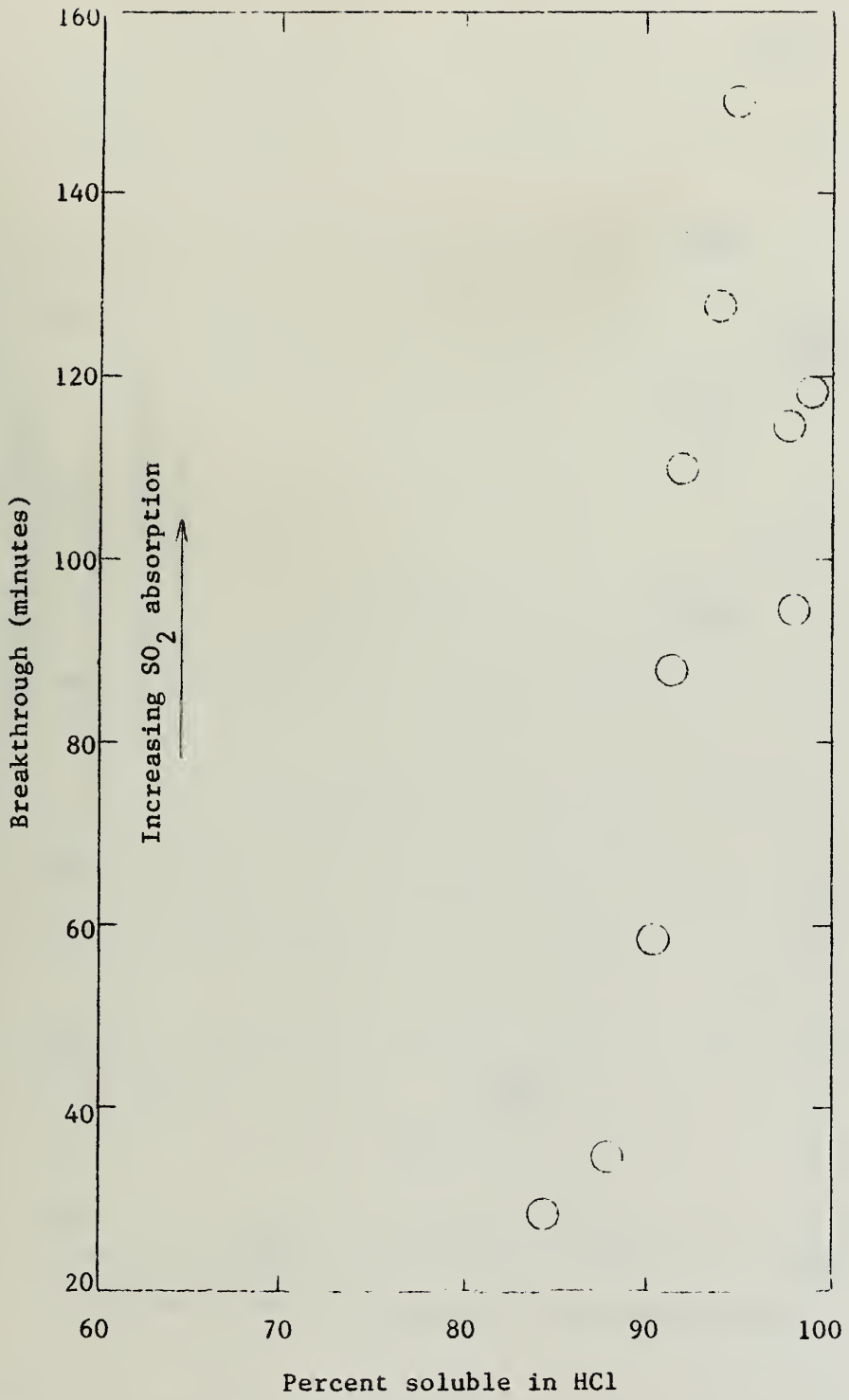

Fig. 2 - Breakthrough time versus percentage soluble in warm hydrochloric acid.

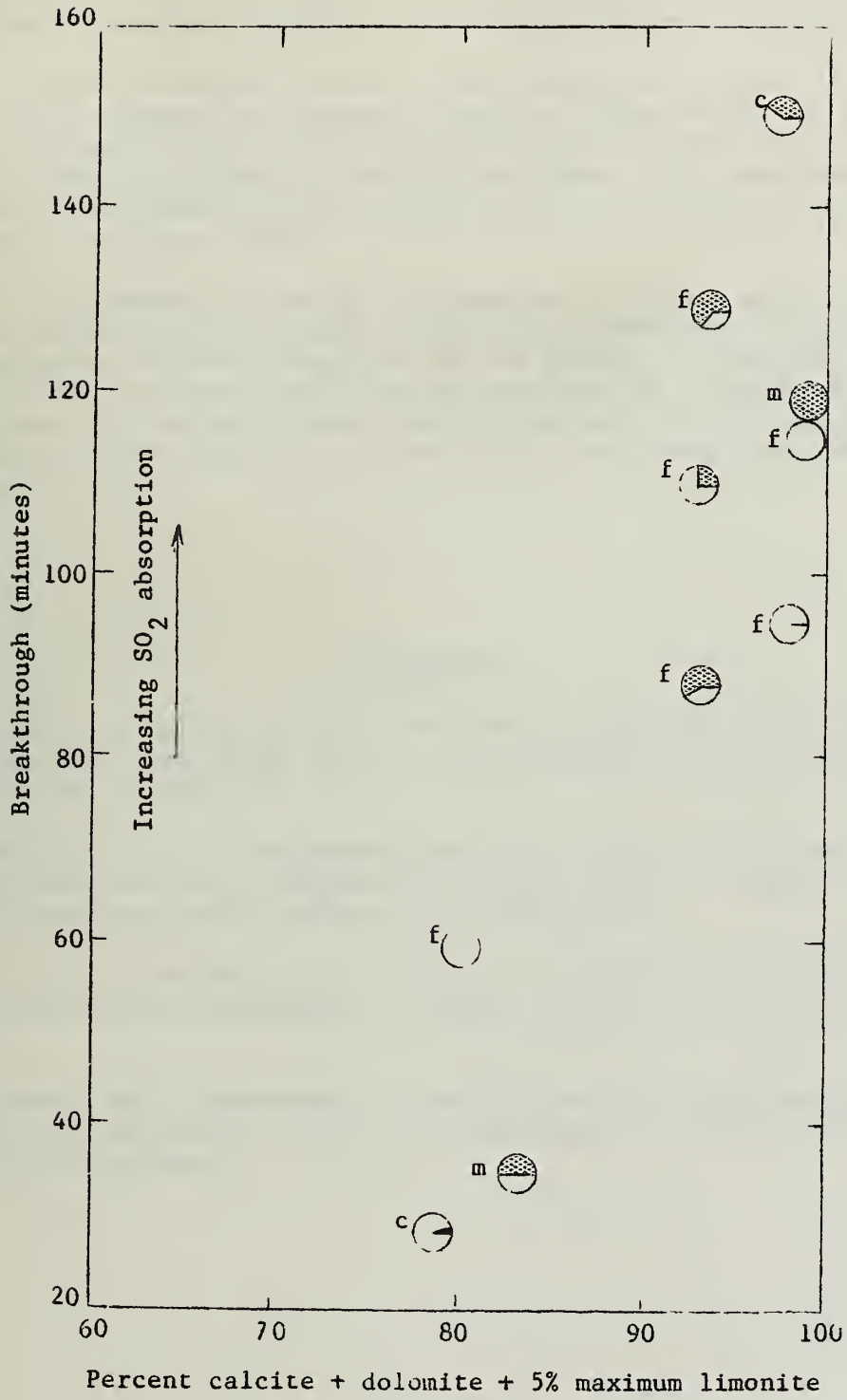

Fig. 3 - Breakthrough time versus the sum of the percentage of calcite, dolomite, and up to 5 percent maximum limonite. Percentage of dolomite is indicated by the shaded area. Grain size is indicated by f (fine), m (medium), and c (coarse).

medium-grained sample (BCR 1337) had an intermediate breakthrough time. However, the most impure samples failed to show this grain-size correlation.

Other petrographic observations affecting SO_2 reactivity are speculative. The occurrence of limonite along many grain boundaries in BCR 1351 reduces the cohesion between dolomite grains, which possibly was a factor in this calcitic dolomites's having a high SO_2 reactivity. The occurrence of an organic film along grain boundaries also possibly tends to increase the reactivity of the stone for the same reason.

The spread of from 30 to 50 minutes in breakthrough time for samples of similar mineral content (figs. 2 and 3) is noteworthy. That it possibly is due to different textural properties in the samples is suggested by the grain-size—SO_2 absorption correlation of the pure samples. Further work along this line may lead to a method of narrowing this spread, which would enable us to give a more accurate prediction of the sulfur reactivity from mineralogical and petrographic data.

REFERENCES

Battelle Memorial Institute, 1966, Fundamental study of sulfur fixation by lime and magnesia: Final Rept. on U. S. Public Health Service Contract No. PH 86-66-108, June 30.

Harrington, R. E., R. H. Borgwardt, and A. E. Potter, 1967, Reactivity of selected limestones and dolomites with sulfur dioxide: American Industrial Hygiene Conf. Ann. Mtg., Chicago, Ill., May 1967.

Rees, O. W., N. F. Shimp, C. W. Beeler, J. K. Kuhn, and R. J. Helfinstine, 1966, Sulfur retention in bituminous coal ash: Illinois Geol. Survey Circ. 396, 10 p.

Wickert, Kurt, 1963, Experiments on desulfurization before and after the burner for reducing the release of SO_2: Mitteilungen der VGB No. 83 (April), p. 74-82. (In German.)

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